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6 COMPLEX FORMATION IN RDX, MHK, TNT, AND
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S. BULUSU

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
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DOVER, NEW JERSEY

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The complexing behavior of energetic materials has begun to emerge as a subject of importance to those involved in the formulation of explosive and propellant compositions. Casting, rheological, and detonation or burning properties of compositions can be affected by the incorporation, deliberately or accidentally, of complexes involving energetic compounds. All too often the nature of the forces which bind the components of the complex is not understood.		

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and cannot be exploited. This bibliography gathers together the known literature references to complexes involving RDX, HMX, and TNT, as well as some related nitramines and nitroaromatics. Because the suspicion exists that crystals of RDX and HMX are at least partially bound together by charge-transfer complexing forces, references to the known crystal structures of the RDX, HMX, and TNT polymorphs are included. In recent years the crystal structures of some of the intermediates in RDX and HMX synthesis have been determined, and references to these structures are also included.

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TABLE OF CONTENTS

	Page No.
Introduction	1
Crystal Structures of some of the RDX, HMX, and TNT Polymorphs	3
Crystal Structures of some Intermediates in RDX and HMX Synthesis	6
Complexes Involving RDX, HMX, or TNT	9
Complexes Involving Other Nitramines or Other Aromatic Nitro Compounds	14
Author Index	21
Distribution List	23

INTRODUCTION

For years the compounds 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) have found extensive use as military explosives. More recently they have been considered for use in low vulnerability propellant (LOVP) formulations. However, workers in both the explosive and propellant areas have encountered certain undesirable properties in formulations containing these materials. For example, the explosive formulation known as Composition B suffers from rheological problems due to the fact that it is a heterogeneous system consisting of RDX crystals embedded in a TNT matrix. Similarly, the LOVP formulations containing HMX show undesirable burning rate characteristics. Formulators have begun to suspect that some of these problems might be alleviated if the nitramine component were combined chemically with other compounds, as, for example, in a molecular complex.

Since the first mention in 1956 (13) of a 1:1 molecular complex involving HMX and dimethylformamide (DMF), complexes of HMX with a large number of other compounds have been prepared by Selig (19-21). These compounds range from open chain N-alkyl amides to amino-benzene and -naphthalene derivatives, phenols, naphthols, cyclic ketones, lactones, heterocyclics such as substituted pyridines, pyridones, quinolones, and finally, phosphoramides. Besides many stable adducts such as the 1:1 HMX-DMF complex, several labile ones have been obtained, e.g., between HMX and γ -butyrolactone or N,N-dimethylaniline.

RDX and HMX can be considered to be mildly acidic in the sense that they can be titrated in nonaqueous solution, and show three or four inflection points respectively, according to the number of nitramine groups in the molecule (*). The majority of the compounds with which HMX forms complexes are mild Brønsted bases (many of them are N-heterocyclic compounds with nonbonding electrons which can participate in charge-transfer reactions, making them basic in the Lewis sense also). Thus, the HMX complexes are also acid-base pairs.

However, an equivalent set of RDX-base pairs apparently does not exist, because RDX does not form complexes with any of the above compounds, with the exceptions of hexamethylphosphortriamide (15), and sulfolane (16). This situation has a parallel in the ability of HMX to crystallize in any of four relatively stable crystal structures (polymorphs), whereas RDX has only one stable structure (there exists a second, unstable polymorph, whose crystallographic structure has not been determined). Stals (+) and Marinkas (**) have suggested

that charge-transfer forces are important factors in the binding energy of the RDX and HMX crystals, and that the crystals are, in fact, self-complexes. If this is so, then the ability of HMX to form polymorphs is simply a special case of its ability to form a variety of complexes.

The geometry of the HMX molecule is not the same in all of its crystal forms (conformational isomerism). It may well be that the ability of the eight-membered HMX ring to assume more than one conformation (e.g., chair or boat form) is the reason for the ability of HMX to form many complexes and to assume several crystal structures in its pure form. This hypothesis is supported by the fact that the compound known as TAT, an analog of HMX which has acetyl instead of nitro groups attached to the eight-membered ring, exhibits both conformational isomerism and polymorphism, while the six-membered analog, known as TRAT, does not.

There appears to be no clear understanding of the nature of the molecular association in the complexes of RDX and HMX. Rather, authors have been willing to assert what type the interaction is not; thus Cobbley and Small (22) conclude that the HMX-DMF complex is not a clathrate, and Castelli, et al. (17) conclude that hydrogen bonding is not responsible. The absence of an absorption band characteristic of the complex and not of either of the components has been used to argue against a charge-transfer nature for the complexes; however Marinkas (**) has suggested that CT bands involving heterocyclic nitramines may be very weak. They may, therefore, have escaped notice. An understanding of the intermolecular binding forces in nitramine complexes could be of great value in the search for ways to combine them with other energetic materials.

Additional clues to the nature of the intermolecular forces may possibly be found in the crystal structures of compounds related to RDX and HMX. These analogs are intermediates in the synthesis of RDX and HMX, and contain other substituents in place of some or all of the nitro groups.

Aromatic nitro compounds, including TNT, have long been known to form complexes with aromatic polyacenes such as anthracene. In these complexes, the intermolecular binding is known to be of charge-transfer nature. Interestingly enough, crystalline TNT is known to exist in any of seven polymorphic forms. The complex formation of polynitro aromatic compounds with ethylenediamine and other bases may also be due to CT interaction (++), as well as the N-methyl pyridone hydroquinone type complexes reported by Thyagarajan, et al. (#).

This bibliography makes no pretense of describing the complexing behavior of all energetic materials. Rather, it is concerned only with complexes of nitroaromatics (including TNT), in which the complexing force is known to be of charge-transfer nature, and with those involving RDX or HMX, in which the complexing force is not understood. To this end, we have referenced the crystal structures of the stable RDX, HMX, and TNT polymorphs (where known), in section starting on page 3; the crystal structures of some of the intermediates in RDX and HMX synthesis in section starting on page 6; crystal structures and/or other data on complexes involving RDX, HMX, or TNT in section starting on page 9; and crystal structures and/or other data on complexes involving other nitramines or other nitroaromatic compounds in section starting on page 14.

It is hoped that this bibliography will serve as a source of background information for those interested in the nature of the forces which link these energetic materials to other compounds, whether that interest be for its own sake, or as an aid to formulation of improved explosives, propellants, or pyrotechnics.

- (*) S. Kaye, *Analytical Chemistry* 27, 292 (1955).
- (**) P.L. Marinkas, *Journal of Luminescence*, 15, 57 (1977) and
P.L. Marinkas, D.S. Downs, J.E. Mapes, P.J. Kemmey, and A.C.
Forsyth, *Molecular Crystals and Liquid Crystals* 35, 15 (1976)
- (+) J. Stals, *Transactions of the Faraday Society*, 67, 1739 (1969).
- (++) D.J. Glover, and E.G. Kayser, *Analytical Chemistry* 40, 2055
(1968).
- (#) B.S. Thyagarajan, et al., *Chemistry and Industry*, November 1966,
p. 1887.

CRYSTAL STRUCTURES OF SOME OF THE RDX, HMX, AND TNT POLYMORPHS

1. Choi, C.S., and E. Prince

"The Crystal Structure of Cyclotrimethylene-trinitramine"

Acta Cryst. 1972, B28, 2857-2862

The structure of cyclotrimethylene-trinitramine (RDX), $C_3H_6N_6O_6$ has been refined from single-crystal neutron-diffraction data. The final weighted *R* index for 836 independent reflections is 0.021. The

Compound crystallizes in the orthorhombic space group $Pbca$, $a=13\cdot182(2)$, $b=11\cdot574(2)$, $c=10\cdot709(2)$ Å, $Z=8$. The molecule consists of alternate CH_2 and $\text{N}-\text{NO}_2$ groups in a puckered ring. The environment of the carbon atoms is essentially tetrahedral, and the $\text{N}-\text{NO}_2$ groups are planar. The molecule possesses a plane of approximate mirror symmetry perpendicular to the plane defined by the three carbon atoms. The thermal motion may be described by rigid-body motion of the ring and separate rigid-body motion of the nitro groups.

2. McCrone, W.C.

"Crystallographic Data, RDX (Cyclotrimethylenetrinitramine)"

Anal. Chem. 1950, 22, 954

RDX is the symbol for the high explosive cyclotrimethylene-trinitramine, which was developed for use during World War II. It can be crystallized from a variety of solvents including benzene, nitromethane, acetone, acetic acid, and nitric acid. It possesses one very unstable polymorphic form (II), which can be isolated only in small quantities for a few seconds during fusion studies on a microscope slide. Because of its physical instability there is no possibility of obtaining RDX II even in laboratory recrystallizations.

3. Cady, H.H., A.C. Larson, and D.T. Cromer

Acta Cryst. 1963, 16, 617

"The Crystal Structure of α -HMX and a Refinement of the Structure of β -HMX"

The crystal structure of the α form of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, commonly known as cyclotetramethylene-tetranitramine or α -HMX, has been determined by single-crystal X-ray methods. The unit cell is orthohombic, space group $Fdd2$ with

$$a=15\cdot14, b=23\cdot89, c=5\cdot913 \text{ \AA}.$$

There are eight molecules in the unit cell. The molecules have a basketlike shape with twofold symmetry. Bond lengths and angles all have normal values, but there are two rather short intermolecular C-O distances of 3.04 and 3.20 Å.

4. Choi, C.S., and H. P. Boutin

Acta Cryst. 1970, B26, 1235

"A Study of the Crystal Structure of β -Cyclotetramethylene-tetrinitramine by Neutron Diffraction"

The crystal structure of β -cyclotetramethylene-tetrinitramine has been reinvestigated by means of neutron diffraction. Least-square refinement of all positional and anisotropic thermal parameters with 545 non-zero reflections yielded a final R value of 0.059. The heavy-atom parameters obtained agree with those from X-ray determinations except for slight position shifts of a few atoms. The positions of the hydrogen atoms have been determined for the first time. All hydrogen atoms are located close to nearby oxygen atoms, a few of which form intramolecular or intermolecular hydrogen bonds of the type C-H...O. Several short intramolecular and intermolecular distances between oxygen and other atoms have been measured.

5. Cobbleyick, R.E., and R. W. H. Small

Acta Cryst. 1974, B30, 1918

"The Crystal Structure of the δ -form of 1,3,5,7-tetraazido 1,3,5,7-tetraaza cyclooctane (δ -HMX)"

The crystal structure of the title compound, $C_4H_8N_8O_8$, has been determined by direct methods from counter intensities. The crystals are hexagonal, space group $P\bar{6}_1$ ($P\bar{6}_5$), with $a=7.711$ (2), $c=32.553$ (6) Å, and $Z=6$. The final R was 0.115 for 1126 observed reflexions. The four C atoms of the eight-membered ring are planar and the molecule has approximate twofold symmetry about an axis perpendicular to this plane through the centre of the ring. The shape of the molecule is similar to that of the α -polymorph which has crystallographic twofold symmetry.

6. Burkhardt, L. A., and J. Bryden

NavOrd Report 2054, 1953

"X-Ray Studies of the Morphology of 2,4,6-Trinitrotoluene"

This study shows 2,4,6-trinitrotoluene to be polymorphic. Seven types have been found to exist, four monoclinic and three orthorhombic. The distinguishing differences between these types exist along the direction of the a -axis. One of the monoclinic forms is produced when

the crystallization of TNT takes place within a few degrees of its melting point. Ordinary crystallization methods produce mixtures, predominately the monoclinic forms. The orthorhombic forms have been obtained by crystallization at -70°C. An explanation of the manner in which these types of TNT differ structurally awaits the determination of the structure of at least one of the forms of TNT.

CRYSTAL STRUCTURES OF SOME INTERMEDIATES IN RDX AND HMX SYNTHESIS

7. Duckworth, J.A.K., B.T.M. Willis, and G.S. Pawley

Acta Cryst. 1970, A26, 263

"Neutron Diffraction Study of the Atomic and Molecular Motion in Hexamethylenetetramine"

An accurate neutron diffraction study has been carried out on a single crystal of hexamethylenetetramine and the measured Bragg intensities have been analysed for the effects of thermal motion. Four different models of the thermal motion have been used in a least-squares refinement of the data: (1) conventional model with ellipsoidal atomic probability density functions; (2) cumulant expansion model with the thermal motion of each atom represented by both second and third cumulant coefficients; (3) as model (1) but including the restriction imposed on the temperature factors by assuming rigid-body molecular motion; (4) as model (2) but including the rigid-body restriction. The best fit is given by model (2), which takes into account deviations from the ellipsoidal atomic probability density functions brought about by libration. Of the rigid-body models, refinement is better for (4) than for (3). Two parameters only $\langle \mu^2 \rangle$ and $\langle \omega^2 \rangle$ of paper I (Willis & Pawley, *Acta Cryst.* (1970), A26, 254) are needed to specify the atomic thermal motions for models (3) and (4), whereas nine parameters are required for model (1) and twenty for model (2). The lone-pair electrons of the nitrogen atom have been detected by combining, in a difference Fourier synthesis, the present data with the X-ray measurements of Becka & Cruickshank (*Proc. Roy. Soc. A* (1963), 273, 435).

8. Choi, C.S., A. Santore, and P.L. Marinkas

Acta Cryst. 1975, B31, 2934

"Crystal Structure of 1,3,5-Triacetyl-2,4,6-hexahydro-s-triazine (TRAT)"

$C_9H_{15}N_3O_3$, monoclinic, $P2_1/c$, $a=7.772(2)$, $b=15.521(4)$, $c=10.101(2)$ Å, $\beta=116.34(2)^\circ$, $Z=4$, $D_x=1.30$, $D_m=1.31$ g cm⁻³, $F(000)=456$. All X-ray measurements were made with MoK^α radiation ($\lambda = 0.71069$ Å). The structure was solved by direct methods and refined by full-matrix least-squares to final R and R_w values of 0.051 and 0.035, respectively, for 777 observed reflections.

9. Choi, C.S., J. E. Abel, B. Dickens, and J.M. Stewart

Acta Cryst. 1973, B29, 651

"The Crystal Structure of 1,3,5,7-Tetraceto-1,3,5,7-tetrazacyclooctane"

The crystal of 1,3,5,7-tetraceto-1,3,5,7-tetrazacyclo-octane, $C_{12}N_4O_4H_{20}$, is tetragonal, $a=b=10.540(2)$ and $c=12.137(3)$ Å, with 4 molecules per unit cell. Systematic absences are consistent with space group $P4_12_12$ (enantiomorphous to $P4_32_12$). The structure was solved by direct methods and refined to a final R index $R_w=0.037$ and $R=0.039$ for 1244 observed reflections. The molecule consists of alternate CH_2 and $N-CO-CH_3$ groups in a puckered C-N ring, having a boat shape conformation with a twofold rotation axis through the center of the C-N ring and perpendicular to the mean plane of the puckered ring. The heavy atoms of each acetyl group are essentially coplanar with its neighbouring nitrogen atom. The molecular thermal motion may be represented chiefly by three motions; a libration about the twofold rotation axis and two intramolecular bending motions about the C-C diagonal of the C-N ring.

10. Choi, C.S., A. Santoro, and J. E. Abel

Acta Cryst. 1976, B32, 354

"The Crystal Structure of 3,7-Diacetyl-1,3,5,7-tetraazabicyclo(3,3,1) nonane (DAPT)"

The crystal structure of 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3,3,1] nonane (DAPT), $C_9H_{16}N_4O_2$, has been determined by single crystal X-ray diffraction techniques. The compound crystallizes in the monoclinic system with $a=6.183(2)$, $b=10.101(2)$, $c=17.037(4)$ Å, $\beta=101.78(4)^\circ$, space group $P2_1/c$, $D_x=1.353$, $D_m=1.34$ g cm⁻³ and $Z=4$. The structure has been solved by direct methods and has been refined by least-squares analysis to a conventional R value of 0.052

($R_{\text{w}} = 0.04$) based on 1708 observed reflections. The molecule of DAPT has a twin-chair conformation similar to that of the molecule of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DPT). The heavy atoms of the acetamide groups are essentially coplanar with the ring carbon atoms adjacent to each group. The bicyclononane ring of the DAPT molecule possesses two pseudo-symmetry planes almost perpendicular to one another. Short intermolecular contacts of 3.28, 3.39 and 3.47 Å have been observed. The molecules having these contacts are stacked along the unique b axis to form a linear chain. The lateral links between chains are weak with contacts between heavy atoms longer than 3.5 Å.

11. Santoro, A., C.S. Choi, and J.E. Abel

Acta Cryst. 1975, B31, 2126

"The Crystal Structure of 1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclo-octane (DADN)"

Abstract. $\text{C}_8\text{H}_{14}\text{N}_6\text{O}_6$, monoclinic, $P2_1/c$, $a=7.422(1)$, $b=13.253(2)$, $c=6.156(1)$ Å, $\beta=103.38(1)^\circ$, $Z=2$, $D_x=1.636$, $D_m=1.63$ g/cm⁻³, $F(000)=304$. X-ray intensities were measured with Mo Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares calculations to final R and R_{w} values of 4.1 and 4.8% respectively, for 1149 observed reflections.

12. Choi, C.S., and S. Bulusu

Acta Cryst. 1974, B30, 1576

"The Crystal Structure of Dinitropentamethylenetetramine (DPT)"

The crystal structure of dinitropentamethylenetetramine, or DPT, $\text{C}_5\text{H}_{10}\text{N}_6\text{O}_4$, has been studied by using three-dimensional X-ray (Mo Kα) diffraction data. The unit cell is monoclinic $P2_1/c$, with $a=9.345(5)$, $b=8.284(5)$, $c=11.566(5)$ Å, $\beta=105.6(1)^\circ$ and $Z=4$. The structure was solved by direct methods and refined by full-matrix least-squares methods to a final $R=0.035$, $R_{\text{w}}=0.037$. The two $\text{N}-\text{NO}_2$ groups in a DPT molecule are planar, with the two nitramine carbons out of the plane. The molecule has approximate mirror symmetry bisecting each of the two nitro groups.

COMPLEXES INVOLVING RDX, HMX, OR TNT

13. Armour Research Foundation Report #5 (Final), 12 Dec 56

"Study of Surface Properties of Explosives" Contract DAI-11-022-501-ORD-(P)-32

The unit cell dimensions (of the HMX-DMF solvate) are: a=16.00 A, and c=31.03 A. There are 18 formula weights per unit cell, 18 times $(\text{CH}_2\text{N}_2\text{O}_2)_4 \cdot \text{HCON}(\text{CH}_3)_2$ or 18 times 369.26; 18.065 calculated from the measured density of 1.61. The calculated x-ray density is 1.604. The axial ratio, a:c, = 1: 1.94. These solvate crystals decrepitate on exposure to air at room temperature. The final percentage loss in weight obtained, experimentally, is 19.6% corresponding to a theoretical value of 19.8% if it is assumed that there is 1 dimethylformamide molecule per 1 HMX molecule. The ultimate desolvated product was determined to be a fine powder of β -HMX-I as determined by powder x-ray diffraction data corresponding to data presented in Table 3 in this report. It is interesting to note that there was relatively little change (or weight loss) in these solvate crystals when they were kept at room temperature under vacuum; there was a gradual loss of weight and gradual change on exposure to the atmosphere at room temperature; and there was a marked accelerated decrepitation when highly humid atmosphere surrounded these crystals at normal room temperature.

14. Brodman, B.W.

J. Appl. Polymer Science, 1976, 20, 2607

"Hydrogen Bonding of HMX and RDX to Unesterified Hydroxyl Groups in Nitrocellulose"

In summary, it has been shown that both HMX and RDX form hydrogen bonds of the OH...O type with unesterified hydroxyl groups in nitrocellulose and an oxygen atom of the respective nitramine, and that RDX forms the stronger bonds.

15. Selig, W.

Explosivstoffe 1966, Vol. 14, No. 8, 174

"A Cyclomethylenetrinitramine:Hexamethylphosphortriamide Complex"

A 1:1 complex of cyclomethylenetrinitramine with hexamethylphosphortriamide was prepared. Some properties of this complex are presented.

16. Michaud, C., H. Marx, G. Poulain, and S. Lepage

Acad. Sc. Paris t267, 1968

"Un Complex de l'Hexogène; Le Complexe 1:1 Hexogène-Sulfolane"

L'hexogène forme un complexe cristallisé 1:1 avec le sulfolane. Il se décompose à 70°C en ses constituants. Il est dissocié dans la plupart des solvants. Ce complexe cristallise dans le système triclinique. Le spectre infrarouge a été étudié.

17. Castelli, A.H., D.J. Cragle, and W.E. Fredericks

Technical Memorandum 1217, Picatinny Arsenal, 1963

"Investigation of Aldehydic Hydrogen Bonding Between Cyclo-tetramethylenetrinitramine (HMX) and Dimethylformamide (DMF)"

The possibility of hydrogen bonding (HB) involving the aldehydic hydrogen (AH) of DMF in the crystalline complex molecule HMX-DMF has been investigated (Part I). Spectroscopic methods were used. DMF-d₁ with deuterium as the AH was employed. The change in the vibrational stretching frequency of the AH of DMF does not indicate that such HB exists in the complex.

Some observations are made concerning variations in intermolecular phenomena between gas and liquid phases of DMF (Part II). Spectroscopic methods were used. HB was found to play no part in these phenomena. The phenomena are explained in terms of a resonance mechanism.

18. Lenchitz, C., and R. Velicky

Technical Memorandum 1343, Picatinny Arsenal, 1964

"A Thermochemical Investigation of the Complex Formed by Cyclotetramethylenetrinitramine (HMX) and Dimethylformamide (DMF)"

The heat of dissociation (ΔH_D) of the complex formed by cyclotetramethylenetrinitramine and dimethylformamide, HMX:DMF, was measured in DMF. ΔH_D for two reactions are reported:

DMF(1)

(a) HMX:DMF(s) \longrightarrow α HMX(s) + DMF(1), 5.2 kcal/mole is absorbed,
DMF(1)
(b) HMX:DMF(s) \longrightarrow β HMX(s) + DMF(1), 4.6 kcal/mole is absorbed.

The difference in crystal energy between α HMX and β HMX as measured in acetone is 0.6 kcal/mole. A mechanism for the solution of HMX in DMF is proposed. The energies measured suggests that the bond forming the complex is due to van der Waals forces. It is also suggested that the dipole - dipole interaction makes a significant contribution to the bond energy.

19. Selig, W.

UCRL 12168, Lawrence Radiation Laboratory, Livermore, California, 1964

"Some 1:1 Complexes of Cyclotetramethylenetrinitramine (HMX) and Their Application to the Estimation of HMX in Admixture with RDX"

1:1 complexes of HMX were prepared with N,N-dimethylformamide, N,N-dimethylpropionamide, N,N-dimethylacetamide, N,N,N',N' tetramethylurea, 1-methyl-2-pyrrolidinone, cyclopentanone, 2-cyclopentenone, 2-cyclohexene-1-one, and γ -butyrolactone. Infrared spectra, x-ray data, differential thermal analysis, and photomicrographs of the complexes are presented.

RDX does not complex with any of the compounds, hence a simple method for the estimation of HMX in admixture with RDX is available.

20. Selig, W.

Explosivstoffe 1967, Vol. 15, No. 4, 76

"Some Complexes of Cyclomethylenetetrinitramine (HMX)"

A variety of organic materials likely to complex HMX was extensively screened. As a result, ten new complexes of HMX were discovered. Equimolar complexes were formed with 2-pyrrolidone, 1,5-dimethyl-2-pyrrolidone, 2-piperidone, N-methyl-2-piperidone, N-vinyl-2-pyrrolidone, N-acetyl-2-pyrrolidone, and octamethylpyrophoramide, N-methyl-2-quinolone formed a 3:2 complex with HMX; N-methyl-2-pyridone and hexamethylphosphortriamide formed 2:1 complexes with HMX.

Some properties useful in the characterization of the complexes are presented.

21. Selig, W.

Explosivstoffe 1969, Vol. 17, No. 4, 73

"Adducts of 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX) III: Adducts with Benzene and Naphthalene Derivatives"

A variety of organic compounds likely to form adducts with HMX were screened, resulting in the discovery of a new series of stable and some labile HMX adducts. These adducts were formed with benzene and naphthalene derivatives containing amino and phenolic groups. Some properties useful in their characterization are presented. In no instance was 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) found to form similar adducts; therefore, HMX may be easily separated from RDX.

22. Cobbleyick, R.E., and R.W.H. Small

Acta Cryst. 1975, B31, 2805

"The Crystal Structure of the Complex Formed Between 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX) and N,N-Dimethylformamide (DMF)"

The crystal structure of $C_4H_8N_8O_8 \cdot C_3H_7NO$ has been determined by direct methods with countermeasured X-ray data. The crystals are rhombohedral, space group $R\bar{3}c$ or $R3c$ with hexagonal cell dimensions $a=15.989(8)$, $c=30.920(12)$ Å and 18 molecules of HMX and DMF in the hexagonal unit cell. The final R was 0.063 for 1521 observed reflections assuming space group $R\bar{3}c$. The HMX molecule has crystallographic twofold symmetry and is similar in shape to the α and δ polymorphs. The DMF molecules are disordered and the closest contacts between HMX and DMF molecules are between CH_2 groups and the carbonyl O atom.

23. Burkhardt, L.A.

Anal. Chem. 1956, 28, 1271

"X-Ray Powder Diffraction Data of Some Molecular Complexes of TNT"

X-ray diffraction patterns are a useful means of characterizing crystalline compounds. During the course of studies of binary systems containing 2,4,6-trinitrotoluene, diffraction data have been accumulated on a number of 2,4,6-trinitrotoluene complexes and constituent compounds.

24. Parihar, D.B., S.P. Sharma, and K.K. Verma

Explosivstoffe 1968, Vol. 16, No. 12, p. 281 and J. Forens. Sci. 1968, 13, 246

"Trace Analysis of Explosives as Pi Complexes"

A rapid and convenient procedure for the identification of as little as 1 to 2 µg of explosives has been described. Nitroaromatic compounds being π acceptors form highly colored charge transfer complexes with aromatic amines (π donors). Thin-layer chromatography of the complexes provides data permitting identification of the explosive. R_F values for ten explosives using three aromatic amines and several solvent systems are given.

COMPLEXES INVOLVING OTHER NITRAMINES
OR OTHER AROMATIC NITRO COMPOUNDS

25. Cobbleyick, R.E., and R.W.H. Small

Acta Cryst. 1973, B29, 640

"The Crystallography of Nitramine-Solvent Complexes. II.
Classification and Crystallographic Data of Some Complexes of 1,7-
Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane (BSX)"

Crystallographic data of some further complexes of the title compound with organic solvents are given. The complexes are classified into types depending on the internal symmetry within the crystals.

26. Cobbleyick, R.E., and R.W.H. Small

Acta Cryst. 1973, B29, 1659

"The Crystallography of Nitramine-Solvent Complexes. III.
The Crystal Structure of the 1:1 Molecular Complex Formed by 1,7-
Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and N,N-Dimethyl-
formamide"

The crystal structure of the 1:1 molecular complex formed by 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and *N,N*-dimethyl-formamide (BSX-DMF) has been determined from three-dimensional X-ray diffraction data. Positional and anisotropic thermal vibrational parameters have been refined by least-squares methods giving a final *R* of 0.066. The crystals are monoclinic, space group $P2_1/n$ with $a=15.359(3)$, $b=19.789(4)$, $c=6.412(2)$ Å, $\beta=97.22(5)^\circ$ and $Z=4$. The structure consists of parallel columns of BSX dimers and channels in which the DMF molecules fit. The complex does not appear to be of the clathrate type; there are close contacts 2.893 and 2.989 Å between nitrogens of adjacent nitro groups of one BSX molecule and a carbonyl oxygen of its centrosymmetric pair. Similar approaches, 2.891 and 2.969 Å, also occur between adjacent nitro nitrogens and the DMF carbonyl oxygen atoms.

27. Herbstein, F.H., and M. Kaftory

Acta Cryst. 1975, B31, 60

"Crystallography of Equimolar Aromatic Hydrocarbon: 1-X-2,4,6-Trinitrobenzene Molecular Compounds. Crystal Structure of Fluoranthrene:picryl Bromide, Polymorph I"

Crystal data are reported for the binary π -molecular compounds with naphthalene, anthracene, phenanthrene, acenaphthlene, fluoranthene, pyrene or triphenylene as donor and 1,3,5-trinitrotetrazene, picric acid, picryl chloride or picryl bromide as acceptor (33 different crystals have been studied). In three out of seven pairs, the trinitrobenzene and picric acid molecular compounds of a particular hydrocarbon are isomorphous, and in four out of seven pairs the picryl chloride and picryl bromide molecular compounds are isomorphous. The structure of fluoranthene:picryl bromide, polymorph I [monoclinic; $a=7.664(8)$, $b=8.035(2)$, $c=31.631(8)$ Å, $\beta=91.8(1)^\circ$, space group $P2_1/c$, $Z=4$] has been solved by Patterson and Fourier methods and refined by block-diagonal least-squares calculations to a final R of 0.062. The structure consists of quasi-hexagonally close-packed mixed stacks of alternating donor and acceptor molecules. The stack axes are parallel to [100]. The interplanar spacing is 3.49 Å, suggesting a rather weak charge-transfer interaction.

28. Brown, D.S., S.C. Wallwork, and W.A. Wilson

Acta Cryst 1964, 17, 168

"The Crystal Structure of the Anthracene-*s*-trinitrobenzene Complex"

The crystal structure of the 1:1 complex formed between anthracene and *s*-trinitrobenzene has been determined at room temperature and at low temperature (*ca.* - 100°C). The structure is basically the same at the two temperatures though there are small differences in atomic positions. The crystals are monoclinic with four molecules of complex in a cell of dimensions $a=11.70$, $b=16.20$, $c=13.22$, $\alpha=11\pm0.02$ Å, $\beta=132.8^\circ\pm0.5^\circ$ at room temperature, and $a=11.35$, $b=16.27$, $c=13.02$, $\alpha=11\pm0.02$ Å, $\beta=133.2^\circ\pm0.5^\circ$ at low temperature, giving the maximum contraction approximately along the [103] crystal direction. The space group is $C2/c$. The structure has been determined at each temperature by three-dimensional Fourier and least-squares methods. The component molecules are stacked alternately, each in two different orientations, in infinite columns along the c axis and the most important intermolecular contacts are approximately along this direction.

29. Hanson, A.W.

Acta Cryst. 1964, 17, 559

"The Crystal Structures of the 1:1 Complexes of Skatole and Indole with *s*-Trinitrobenzene"

Crystals of complexes of both skatole and indole with *s*-trinitrobenzene are monoclinic, P_{2_1}/a , with $Z=4$. Unit-cell constants at -140°C are, for the skatole complex:

$$a=16.76, b=6.61, c=13.45 \text{ \AA}; \beta=95.6^\circ,$$

and the indole complex:

$$a=15.87, b=6.58, c=13.47 \text{ \AA}; \beta=94.8^\circ.$$

The crystal structure of the skatole complex was determined by inspection of certain sections of the three-dimensional Patterson synthesis, and refined with the aid of three-dimensional Fourier and differential syntheses. The crystal structure of the indole complex was solved by analogy with that of the skatole complex, but was found to be disordered, with the indole molecule capable of assuming two alternative orientations. It was refined with the aid of three-dimensional Fourier syntheses and bounded projections.

Both skatole and indole molecules are planar, to the accuracy of the analyses, but the *s*-trinitrobenzene molecule is not. The NO_2 groups are twisted out of the plane of the benzene nucleus by amounts which vary, and which are probably governed by molecular packing.

The constituent molecules overlap each other with an average interplanar spacing of 3.30 \AA . The relative orientations in all cases suggest a decisive attraction between a non-substituted (2,4,6) carbon position of the *s*-trinitrobenzene molecule, and the nitrogen atom of the skatole or indole molecule.

30. Hanson, A.W.

Acta Cryst. 1965, 19, 19

"The Crystal Structure of the Azulene *s*-Trinitrobenzene Complex"

The crystal is monoclinic P_{2_1}/a , with $Z=4$. Unit-cell constants at -95°C are $a=16.39, b=6.66, c=13.77 \text{ \AA}, \beta=96.10^\circ$. The formula is $\text{C}_{10}\text{H}_8\text{C}_6\text{H}_3\text{N}_3\text{O}_6$.

The structure was determined from the three-dimensional Patterson synthesis, and refined by least-squares procedures. The structure is disordered, with about 7% of the azulene molecules adopting an alternative orientation, but this disorder did not seriously limit the accuracy of the analysis.

The azulene molecule is nearly planar, but the *s*-trinitrobenzene molecule is not. The NO₂ groups are twisted out of the plane of the benzene nucleus by amounts which vary, and which are probably determined by molecular environment. The constituent molecules overlap each other with an average interplanar spacing of 3.33 Å, but two C-N contacts are found to have lengths of 3.30 Å.

31. Hanson, A.W.

Acta Cryst. 1966, 21, 97

"The Crystal Structure of the Acepleiadylene *s*-Trinitrobenzene Complex"

The crystal is triclinic, probably $\overline{P1}$, with $Z=2$. Unit-cell constants at -150°C are $a=8.791$, $b=16.055$, $c=6.515$, $\alpha=92.87$, $\beta=102.18$, $\gamma=98.98^\circ$. The formula is $C_{16}H_{10} \cdot C_6H_3N_3O_6$.

The structure was determined from the three-dimensional Patterson synthesis. It was refined by Fourier and differential syntheses, and finally by least-squares procedures.

Both molecules are significantly non-planar. They overlap each other with an average interplanar spacing of 3.26 Å, but a carbon-nitrogen distance of 3.20 Å and a carbon-carbon distance of 3.24 Å also occur.

32. Carter, O.L., A.T. McPhail, and G.A. Sim

J. Chem. Soc. (A) 1966, p. 822

"Crystal and Molecular Structure of the Tricarbonylchromiumanisole *s*-1,3,5-Trinitrobenzene Complex"

Crystals of the 1:1 electron donor-acceptor complex formed from tricarbonylchromiumanisole and 1,3,5-trinitrobenzene are monoclinic, space group $P2_1/c$, with $a=10.10$, $b=13.42$, $c=13.87$ Å, $\beta=101^\circ 45'$, $Z=4$. A three-dimensional single-crystal X-ray analysis has shown

that the benzene rings of the two components are inclined at 3°, that is, they are very nearly parallel, with perpendicular distances from the aromatic carbon atoms of the anisole molecule to the plane of the trinitrobenzene molecule ranging from 3.34 to 3.50 Å (average 3.41 Å). The benzene rings of the anisole and trinitrobenzene molecules are tilted by 24 and 27°, respectively, out of the orientation perpendicular to the line joining the centres of the rings. In the trinitrobenzene component the ring valency angles at the carbon atoms carrying nitro-groups (123°) are significantly greater than the valency angles at the other carbon atoms (117°); an explanation based on σ-bond hybridisation is suggested.

33. Herbstein, F.H., and M. Kaftory

Acta Cryst. 1976, B32, 387

"Molecular Compounds and Complexes. VII. The Crystal Structure of Anthracene:Picric Acid"

The structure of the π-molecular compound anthracene:picric acid (monoclinic; $a=7.180$, $b=12.901$, $c=19.205$ Å, $\beta=90.52^\circ$, space group $P2_1/c$, $Z=4$) has been solved by direct methods, and refined to $R=5.0\%$ (goodness of fit=1.67) with the intensities of 2092 non-zero reflexions measured on a diffractometer (graphite-monochromatized Mo Kα). The components are arranged alternately in quasi-hexagonally close-packed mixed stacks, extending in the [100] direction. The picric acid molecule has an intramolecular hydrogen bond between the phenol OH group and an adjacent nitro group. The individual six-membered rings of the anthracene molecule are planar but the molecule as a whole deviates significantly from planarity and is also almost but not quite centrosymmetric. The bond lengths and angles conform to $m\bar{m}$ symmetry. The small differences found between the dimensions of anthracene in its picric acid molecular compound and in crystalline anthracene are not statistically significant.

34. Herbstein, F.H., and M. Kaftory

Acta Cryst. 1975, B31, 68

"The Crystal Structure of 3/2 Pyrene:Picryl Bromide"

3/2 Pyrene:picryl bromide, $(C_{16}H_{10})_{3/2}:C_6H_2(NO_2)_3Br$, is monoclinic with $a=8.189(2)$, $b=21.070(6)$, $c=14.607(4)$ Å, $\beta=91.7(1)^\circ$, space group $P2_1/c$, $Z=4$. Intensities of 2893 reflexions were measured on

a Stoe Weissenberg diffractometer with graphite-monochromated Cu $\text{K}\alpha$ radiation. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares calculations to a final R of 0.103. All the atoms have fairly large Debye-Waller factors, suggesting the occurrence of large in-plane librations and/or disorder. The crystal structure can be described in terms of mixed stacks along [001] and interstitial pyrene molecules whose centres lie at $(0,0,1/2)$ and $(0,1/2,0)$. The donor:acceptor arrangement within the stacks is similar to that in anthracene:1,3,5-trinitrobenzene [Brown, Wallwork & Wilson (1964). *Acta Cryst.* 17, 168-176].

35. Selig, W., and B. Mallon

Explosivstoffe 1968, Vol. 16, No. 12, 266

"Some 1:2 Adducts of Tetranitro-2,3:5,6-dibenzo-1,3a,4,6a-tetra-azapentalene (TACOT)"

Twelve 1:2 adducts of tetranitro-2,3:5,6-dibenzo-1,3a,4,6a-tetra-azapentalene (TACOT) were prepared. Labile adducts were formed with N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, and N-methyl-2-pyriperidone. Stable adducts were formed with N-ethyl-2-pyridone, N-n-propyl and N-isopropyl-2-pyridone, N-n-butyl-2-pyridone, N-methyl-2-quinolone, N,N-dimethylnicotinamide, N,N-dimethylbenzamide, and diphenylsulfoxide. Aromatization and conjugation in the adduct-forming solvents favor formation of stable adducts. Some properties useful in the characterization of the adducts are presented.

AUTHOR INDEX

Abel, J.E.	9,10,11	Larson, A.C.	3
Boutin, H.P.	4	Lenchitz, C.	18
Brodmann, B.W.	14	Lepage, S.	16
Brown, D.S.	28	McCrone, W.C.	2
Bryden, J.	6	Michaud, C.	16
Bulusu, S.	12	McPhail, A.T.	32
Burkhardt, L.A.	6,23	Marinkas, P.L.	**,8
		Marx, H.	16
Cady, H.H.	3	Parihar, D.B.	24
Carter, O.L.	32	Pawley, G.S.	7
Castelli, A.H.	17	Poulain, G.	16
Choi, C.S.	1,4,8,9,10,11,12	Prince, E.	1
Cobbledick, R.E.	5,22,25,26	Santoro, A.	8,10,11
Cragle, D.J.	17	Selig, W.	15,19,20,21,35
Cromer, D.T.	3	Sharma, S.P.	24
Dickens, B.	9	Sim, G.A.	32
Duckworth, J.A.K.	7	Small, R.W.H.	22,25,26
Fredericks, W.E.	17	Stals, J.	+
Glover, D.J.	++	Stewart, J.M.	9
Hanson, A.W.	29,30,31	Thyagarajan, B.S.	#
Herbstein, F.H.	27,33,34	Velicky, R.	18
Kayser, E.G.	++	Verma, K.K.	24
Kaye, S.	*	Willis, B.T.M.	7
Kaftory, M.	27,33,34	Wilson, W.A.	28
		Wallwork, S.C.	28

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Mr. C. Lenchitz	32
Mr. T. Boxer	33
Dr. Z. Iqbal	34
Dr. P.L. Marinkas	35-59
Dr. S. Bulusu	60-84
Mr. J. E. Abel	85-110
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